A STUDY OF THE SPECTRAL TRANSMISSION OF GLASSES

BY

GEORGE STRICKLER BACHMAN

B.S., Pennsylvania State College, 1936
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B.S.E.(Ch.E.), University of Michigan, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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The analysis of infrared radiation transmitted by various substances can serve as a tool for the determination of their structures. Infrared absorption bands are caused by natural vibrations of the molecules, and the structure of a molecule can sometimes be determined by the presence or absence of bands at points where the different possible structures might absorb.

One aim of this work was to examine the infrared spectra of silicate glasses prepared from crystals whose structures are known in an endeavor to cast some light on the structure of glasses. The present view on the structure of glasses is that of limited order; i. e., the structure consists of an extended three-dimensional network, not entirely random and yet not periodic and symmetrical as in crystals. Each silicon atom is tetrahedrally surrounded by four oxygen atoms, and each of these oxygen atoms may be further shared by another silicon atom, or by aluminum, sodium, calcium, potassium, etc., atoms, depending of course on the composition of the silicate glass. The cations other than silicon (and aluminum in some instances) are regarded as being held rather loosely in the various holes of the silicon-oxygen network. It appears to be generally believed that these cations are evenly distributed throughout the structure, and the consequence of such a view is that the structure of a silicate glass is uniquely determined by its composition.

In order to test the validity of this theory, crystals of the same chemical composition but of different structure

(such as microcline and orthoclase, or albite and anorthoclase) were melted, and infrared transmission curves obtained by the powder method for the resulting glasses, as well as for the original mineral crystals. If the structure of a glass is determined under all circumstances by its composition alone, one would expect the infrared transmission curves for the microline and orthoclase gblasses to be exactly the same—likewise for albite and anorthoclase. If, however, the structure of a glass has some correlation to that of the crystal from which it was melted, one would expect the transmission curves for microline and orthoclase (or albite and anorthoclase) to be somewhat dissimilar, since the infrared transmission curves for the original minerals are somewhat dissimilar.

Our results indicate that the latter of the above views is the corect one, and that glasses of identical composition may vary somewhat in structure. Our results further indicate that the transmissibilities (corrected for thickness of the powder layer) of the glasses at a certain wave-length are in the same order as those of the original crystals—namely, in decreasing order, microcline, anorthoclase, orthoclase, albite. It may be concluded that there is some relationship between the structure of a glass and that of the parent crystal.

Another aim of this work was to determine the influence of the common coloring oxides on the spectral transmission of an ordinary soda-lime-silica glass. The composition of the base glass was similar to that used for containers. The oxides chosen for addition to the base glass were those ionic colorants ordinarily used to color glass, as well as several others which were deemed to be of interest in this investigation. Three rare-earth oxides—namely, neodymium oxide, praseodymium oxide, and samarium oxide—were also used as colorants. The coloring oxides used, their formulas, and the amounts added to the base glass were as follows:

TABLE I

Element added	Oxide addition	Proportion: Wt. of the oxide addition expressed as a percentage of wt. of the base glass. Series 1 %	Series 2 %	Series 3 %
V	V_2O_5	0.500	1.000	2.000
Cr	Cr_2O_3	0.100	0.200	0.500
Cu	CuO	0.500	1.000	2.000
Fe	Fe_2O_3	0.500	1.000	2.000
Co	Co_3O_4	0.020	0.050	0.100
Ni	Ni_2O_3	0.100	0.200	0.500
Nd	Nd_2O_3	1.000	2.000	5.000
Pr	Pr_6O_{11}	1.000	2.000	5.000
Sm	Sm_2O_3	1.000	2.000	5.000
U	U_2O_3	0.500	1.000	2.000

The glasses were melted twice in order to assure homogeneity. The first melting took place in platinum crucibles; the second took place in platinum-rhodium crucibles. On cooling, the glasses separated themselves from the platinum-rhodium crucibles and could be removed in the form of discs. These discs were annealed, ground, and polished.

The spectral transmission of the glass samples prepared in the above manner was determined by means of three different instruments. A Beckman spectrophotometer was used in the ultraviolet region and a small part of the infrared region; a Hardy-G. E. recording spectrophotometer was used in the visible region (400 to 700 millimicrons); a Perkin-Elmer infrared spectrometer was used in the infrared region.

By means of observations in the visible region and the use of the Fresnel reflection formula, reflection losses were determined for each glass. All observed data were corrected for this reflection loss in order to report them on an "internal transmittance" basis.

The complete spectra thus obtained for each glass exhibited absorption bands which may be divided into three classifications: (a) an absorption band at 3.5 to 4.0 microns, due to the structure of the glass itself; (b) an absorption band at about 2.9 microns, due to the water content of the glass; and (c) a series of absorption bands, differing for the different glasses, between the ultraviolet cut-off of the base glass (at about 280 millimicrons) and about 2.6 microns. These may be considered as due to the "electronic" absorption of the atoms of the colorant. Certain electrons in these atoms can absorb energy of a definite frequency from the incident radiation, a process which results in the phenomenon of selective absorption.

Cr_2O_3 and CuO have similar over-all absorption spectra.

The rare-earth oxides—neodymium oxide, praseodymium oxide, and samarium oxide—show the sharp absorption bands characteristic of the rare earths in all three portions of the spectrum—ultraviolet, visible, and infrared.

There was no noticeable variation in the position of the infrared cut-off for all glasses. It was at approximately 4.7 microns.

The ultraviolet cut-off for the base glass was at 280 millimicrons. No other glass had any transmission at wave-lengths less than this figure, and in many cases the cut-offs were at wave-lengths greater than 280 millimicrons, depending on the coloring oxide used and the amount of that oxide added to the base glass.

Co_3O_4 was found to be the most powerful absorbing agent per unit weight in the infrared as well as the visible. Ni_2O_3 is also a better absorbing agent per unit weight than Fe_2O_3 in the infrared. However, both Co_3O_4 and Ni_2O_3 have high absorptions in the visible region also. Fe_2O_3 is the only oxide with high infrared absorption that has a relatively high transmission (i. e., low absorption) in the visible region.

CuO and Cr_2O_3 are the best absorbers in the near infrared region (next to the visible spectrum).

Cr_2O_3 is the best absorber in the ultraviolet. The glass containing 0.50% Cr_2O_3 transmitted no ultraviolet radiation. V_2O_5 is the second best absorber of ultraviolet radiation.

Glasses containing Nd_2O_3, Pr_6O_{11}, Sm_2O_3, V_2O_5, and U_2O_3 have a relatively high over-all transmission of radiant energy.

The glasses followed Beer's Law fairly closely in the visible region.

VITA

George Strickler Bachman was born in Lebanon, Pennsylvania, on January 6, 1915. He received his elementary and high school education in that city, graduating from high school in 1932. After one year at Lebanon Valley College, Annville, Pennsylvania, he matriculated at the Pennsylvania State College, taking the course in Ceramics, School of Mineral Industries. He graduated with honors in 1936, and was appointed to a Graduate Assistantship in order to work for a Master's degree. He completed the work for this degree in the summer of 1937, and was granted the degree in January, 1938. From September, 1937, to November, 1942, he was employed as a ceramic engineer by the Owens-Illinois Glass Company, Alton, Illinois. He was inducted into the Army in November, 1942, and spent the next two years and ten months in service, the latter part of which was spent in the E. T. O. While in service he completed the A. S. T. P. course in Chemical Engineering at the University of Michigan and was granted the degree of B. S. in Engineering by the University in October, 1943. Upon discharge from service in October, 1945, he resumed his former position for several months, and then matriculated at the University of Illinois.

He is a member of the American Ceramic Society, Theta Chi social fraternity, and Keramos, Sigma Xi, Phi Kappa Phi, Tau Beta Pi, and Sigma Gamma Epsilon professional and honorary fraternities. He is a Registered Professional Engineer, State of Illinois.

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